

SINGLE PULSE SHOCK TUBE STUDIES ON THE UNIMOLECULAR
DECOMPOSITION OF LARGE UNSATURATED MOLECULES:
TRANS-1-PHENYL-1-PENTENE

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Introduction

Decomposition kinetics represent an important component of combustion chemistry. A challenging aspect of this chemistry involves the building up, breakdown and rearrangements of large and unsaturated structures. In this paper experiments that lead to quantitative information on the thermodynamic and kinetic properties of these large unstable species will be described. The aim is to provide a base of information upon which predictions can be made. Thus the concentration on single step thermal reactions. Previously, the methodology has been employed to determine unimolecular rate constants (at the high pressure limit) for the decomposition of a large variety of alkenes, alkynes and benzyl compounds. These have also led to a determination of the heat of formation of the large radicals that are formed. A summary of earlier results can be found in Table 1.

	Rate Expressions	Constants (1100)
	s^{-1}	
1-hexene \rightarrow allyl+n-propyl ¹	$8 \times 10^{15} \exp(-35600/T)$	70
\rightarrow 2 propene	$4 \times 10^{12} \exp(-28900/T)$	16
1-hexyne \rightarrow propargyl+n-propyl ¹	$8 \times 10^{15} \exp(-36300/T)$	37
\rightarrow allene+propene	$5 \times 10^{12} \exp(-28400/T)$	31
phenylpentane \rightarrow benzyl+n-butyl ²	$1 \times 10^{16} \exp(-36500/T)$	39
c-hexene-2 \rightarrow t-hexene-2 ³	$4 \times 10^{14} \exp(-33333/T)$	37
t-1,3pentadiene \rightarrow c-1,3pentadiene ⁴	$4 \times 10^{13} \exp(-26700/T)$	287

Table 1. Earlier Data on the Decomposition of Unsaturated Compounds

The present study is concerned with a molecule that contains both aromatic and olefinic groups, trans 1-phenylpentene (TPP). Possible mechanisms for decomposition can be found in Figure 1. They involve the cleavage of the resonance weakened C-C bond (2) leading to the formation of 3-methylallyl radical and ethyl, a retroene reaction (1) that forms ethylene and allylbenzene directly and trans to cis(CPP) isomerization (3). All of these reactions have their counterparts in the simpler compounds. Some of the results are listed in Table 1. The quantitative results will bear on a number of interesting issues. In the case of trans-cis isomerization, it will be possible to determine the effect of benzyl resonance. From the rate expression for bond breaking, the activation energy will lead directly to the heat of formation of the 3-phenylallyl radical and in turn its resonance energy. The A-factor can be compared with that for reactions of the 1-olefins, thus leading to information on the effect of the addition to the phenyl group to the vinyl structure. Of particular interest will be the fate of the 3-phenylallyl radical. It can undergo beta bond scission to form phenyl allene or internal displacement to form indene. The latter is especially interesting since it represents the formation of the second ring in such systems. We have observed indene formation in the hydrogen atom induced decomposition of 1-phenylpropene and for the purposes of determining abstraction rate constants it is important to demonstrate that the conversion is quantitative. Similarly, it will be possible to determine how the rate constants for the molecular, retroene, process will be effected in the more complex environment of this molecule.

Single pulse shock tube studies have unique capabilities for

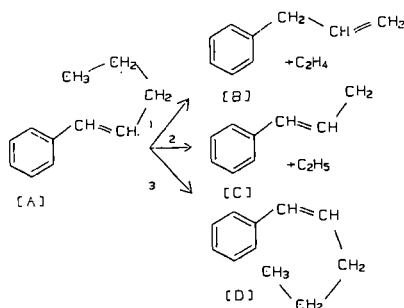


Figure 1. Mechanism for the decomposition of trans-1-phenyl-1-pentene. A=Trans-1-phenyl-1-pentene, B=Allylbenzene, C=3-phenylallyl, D=Cis-1-phenyl-1-pentene

determining the thermal decomposition properties of large organic molecules. There is no chance of surface processes. Final product analysis using gas chromatography with flame ionization detection offers the possibility of detecting all reactants and products. Multiple reaction channels can thus be quantitatively investigated. By working at dilute concentrations, in the presence of a chemical inhibitor, all chain processes can be suppressed. The high temperatures are an important factor in assuring that practically all large organic radicals are decomposed in a time scale such that only the initial and subsequent unimolecular decomposition processes can occur. This is an important aid in the interpretation of the results. The isolation of individual reactions for study means that it is possible to study a number of unimolecular decompositions simultaneously. This is the basis of the internal standard method and removes the uncertainty in the reaction temperature, an important contributing factor to errors in single pulse shock tube experiments. The general technique has been successfully used to determine the rate expression for unimolecular decomposition of many organic compounds. For bond breaking reactions, these lead directly to heats of formation of the organic radicals that are formed. It is by this technique that the first indications were obtained regarding the need for an upgrading of the then generally used heats of formation of simple alkyl radicals⁵.

There have been no previous study on the decomposition of TPP. Robaugh and Stein⁶ have studied in VLLP experiments the decomposition of 1-phenyl-1-butene. Assuming an A-factor of $2 \times 10^{15} \text{ s}^{-1}$, they find an activation energy of 282 kJ/mol leading to an "extra" resonance energy in comparison to that for benzyl of 23 kJ/mol. From the data in Table 1 it can be seen that the breaking of the C-C bond in these cases are characterized by A-factor near 10^{16} s^{-1} and resonance energies near 45 kJ/mol. The former is a factor of 3 smaller than the characteristic values for alkanes while the latter is directly reflected in the activation energy. The smaller A-factor for alkene and alkyne decomposition can be attributed to the tightened structure of the resonance stabilized radical that is formed and contrasts with the alkyl radicals formed during alkane decomposition. Overall, the unimolecular rate constants are increased by factors ranging from 20 to 30 as a result of allylic and benzyl substitution at the present temperatures. For the 3-phenylallyl radical, the structure compared to the molecule is even tighter since two weakly hindered rotors will in the radical become torsions. At these temperatures, retroene reactions are competitive with the bond breaking reaction for the alkenes and alkynes (see Table 1) but apparently does not occur for the benzyl compounds. The recommended rate expressions for the cis \leftrightarrow trans isomerization demonstrate that the full value of the resonance energy is manifested in the transition state. There appears to be

surprisingly large differences in the A-factors. Nevertheless, the changes are in the proper direction.

Experimental

Experiments are carried out in a heated single pulse shock tube. The entire shock tube and the gas handling system is maintained at 100°C. This permits the introduction and withdrawal from the shock tube of quantitative mixtures of low-volatility compounds. Details of the apparatus and the procedures can be found in earlier papers¹. Analysis is by gas chromatography with flame ionization detection. Two columns are used for the analysis. The light hydrocarbons, principally ethylene are separated with a 12 foot Poropak N⁷ column operated at 50 C. For the heavier species, from C₄ on up, a wide bore 30 meter dimethylsiloxalane column in the programmed temperature mode is used for analysis. Toluene is used as the chemical inhibitor. The ratio of toluene to the TPP is maintained at 200 to 1. This guarantees that all the reactive radicals will react with toluene in preference to the TPP. Stable benzyl radicals are formed. Under the conditions of the shock tube experiments they can only recombine with itself or other radicals that are present. They have insufficient time to react with the TPP. As a result the initial unimolecular decomposition reaction is isolated for study. For the determination of rate expressions, the use of an internal standard as the reference reaction¹ ($k(1\text{-methylcyclohexene} \rightarrow \text{isoprene} + \text{ethylene}) = 10^{15} \exp(-33500/T) \text{ s}^{-1}$) permits the calculation of the reaction temperature on the basis of the extent of reaction and the heating time (500 microseconds).

Results

The important products formed from the thermal decomposition of dilute concentrations of TPP in large excesses of toluene are listed in Table I. Also present are considerable amounts of methane and smaller quantities of ethane and ethylbenzene. These are the expected products from the hydrogen atom induced decomposition of toluene. These were not needed for the quantitative analysis of the data. Excellent mass balances are realized and it is clear that the mechanism outlined in Figure 1 fully accounts for the decomposition processes. Benzene is from the reaction of hydrogen atom with toluene and the amount that is formed is in reasonable agreement from that which would have been predicted on the basis of earlier determinations of hydrogen atom attack on toluene. Note that the benzene formed is a measure of all the hydrogen that can be formed in the reactive system. This can include impurities or small quantities from the decomposition of toluene, the inhibitor itself. Ethylene is formed from the decomposition of the ethyl radical and directly from the retroene reaction. From the allylbenzene yields, it is apparent that the latter is only a minor reaction channel. Unfortunately allylbenzene is present as an impurity in the reaction mixture.

Table 2: Typical Product Distribution from the Decomposition of 100 ppm Phenyl-1-Pentene in 2% Toluene at 2 atm. pressure

Compounds	Temperature (K)		
	% yield		
	1057	1080	1149
ethylene	2.7	4.9	27.3
benzene	1.7	3.0	17.2
allylbenzene		.62	1.3
indene	2.2	4.3	24.5
cis-phenyl-1-pentene	4.4	6.6	13.1
trans-phenyl-1-pentene	93.9	88.2	60.4

Thus it proved impossible to make a high accuracy determination of the rate expression of the retroene reaction. Nevertheless it is interesting that, as required, the sum of the allylbenzene and indene concentration is close to that of the ethylene found. Indene and the cis isomer are the major large reaction products.

The former is more important at high extent of reaction. The satisfactory mass balance indicates that all the 3-phenylallyl radical formed is converted into indene. Further confirmation is offered by the absence of any of the phenyl butenes, the expected product from the addition of methyl radicals to 3-phenylallyl. This radical should exist in the cis and trans conformation and it is only from the cis isomerization that indene can be formed. The present results demonstrate that under high temperature conditions this isomerization must be quite rapid. No phenyl allene is detected. Beta bond cleavage is not competitive with internal displacement. This is not surprising since it is expected that the activation energy for the ejection of a beta hydrogen bond in this system will have an activation energy of 260 kJ/mol.

A small uncertainty is introduced into the quantitative interpretation of the results in terms of bond breaking by the simultaneous conversion of TPP to the cis-isomer with the bond breaking reaction. The cis-isomer can of course also undergo the retro-ene and bond breaking reactions. At the high temperatures of these experiments the properties of the cis and trans isomers are very similar. It should be possible to speak of a single average entity. Furthermore, the concentration of the cis compound is never more than 20% of the trans species. On this basis and using the relation $k = \log (1 - X \cdot \text{indene}/(\text{TPP})_i) / X \cdot t$ where t is the residence time of about 500 microseconds and $X = 1 + \text{allylbenzene}/\text{indene}$ and represents the contribution from the retroene channel, an Arrhenius plot of the data can be found in Figure 1. This leads to the following rate expression for the bond breaking reaction $k(\text{TPP} \rightarrow 3\text{-phenylallyl} + \text{ethyl}) = 4 \times 10^{15} \exp(-34010/RT) \text{ s}^{-1}$ over the temperature range of 1000-1180 K. and at a pressure of argon of approximately 2 atms.

As noted earlier, accurate determination of the concentration of allylbenzene is made difficult by its presence as an impurity. The consequence is that it is necessary to subtract two numbers. Thus as can be seen in Figure 1, the data show considerable scatter. The rate expression that is obtained $k(1\text{-PP} \rightarrow \text{allylbenzene} + \text{C}_2\text{H}_4) = 1.9 \times 10^{11} \exp(-25640/T) \text{ s}^{-1}$ has parameters that are much lower than that listed above. Nevertheless, it is probably not an accident that at 1100 K the rate constant is 14 s^{-1} or very close to the value for hexene decomposition to form two propene. It is suspected that the expression in Table 1 is more likely to be the correct one.

From the yields of cis-1-phenylpentene (CPP), the rate expression for trans \rightarrow cis isomerization can be obtained. The rate relation is $k_3 = \log(1(\text{CPP}/\text{TPP})_i) / (1 + K_{eq}) \exp(k_1 + k_2)t / (1 + K_{eq})t = k_3$ where $K_{eq} = k_3/k_{-3}$ and is derived from the observed convergence of the ratio of the trans and cis compounds as the temperature is increased. This ratio, 3.9 implies the greater stability of the trans compounds and is contrary to the published results for the analogous phenylpropenes⁹. An Arrhenius plot of the results can also be found in Figure 1. This leads to the rate expression $1.5 \times 10^{13} \exp(-27400/T) \text{ s}^{-1}$.

Discussion

The experimental rate constants are only slightly larger than that determined by Robaugh and Stein. Since their study involves the ejection of a methyl group instead an ethyl the differences should be somewhat larger. It is suspected that the discrepancies are about a factor of 1.5 to 2. High pressure rate constants are not directly determined from VLPP studies and this type of differences may arise from the extrapolational procedure.

Assuming that combination rate constants involving 3-phenylallyl and ethyl radical have no temperature dependence, the enthalpy of reaction at 1100 K is 291 kJ/mol. From known thermodynamics⁸ this is equivalent to a resonance energy of the 3-phenylallyl radical of $66 \pm 6 \text{ kJ/mol}$ and can be compared with that for allyl and benzyl of about $50 \pm 4 \text{ kJ/mol}$ ¹. The heat of formation of the 3-phenylallyl radical is $228 \pm 6 \text{ kJ/mol}$. The A-factor is an

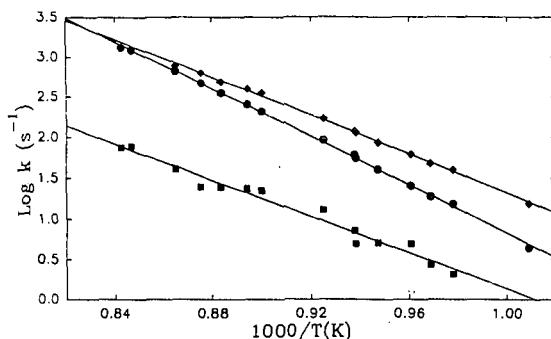


Figure 2: Arrhenius Plots for the Decomposition of t-1-phenylpentene to form 3-phenylallyl + C₂H₅, (●); cis-1-phenylpentene, (◆); and allylbenzene + C₂H₄, (■).

order of magnitude and half an order of magnitude lower than those for alkanes and alkenes, respectively and is consistent with the very stiff radical (no free rotors) that is formed. At lower temperatures rate constants for cis isomerization are larger than that for bond cleavage. They are consistent with an activation energy that feels the full effect of the benzyl resonance energy. The retroene reaction is slower than for bond cleavage. It appears that phenyl substitution does not have much effect on the rate constants. The satisfactory mass balance also means that there are no other processes that make contributions to the decomposition process as the molecular complexity is increased.

The formation of indene from 3-methylallyl must involve an internal addition followed by the displacement of the hydrogen atom. This is an endothermic process. From the heat of formation of 3-methylallyl and indene⁹ the enthalpy of reaction is 63 kJ/mol. When this is coupled with the estimated barrier for addition of hydrogen to indene leading to the breaking of the olefinic ring structure one obtains an overall barrier for cyclization of 89 kJ/mol. This barrier is made up of a barrier to addition and then that for ejection of hydrogen. An actual rate expression could be derived if there are reliable values for the entropies of indene. In its absence, a typical value of the A-factor, 10¹¹s⁻¹, coupled with the barrier for cyclization will lead to rate constants near 0.5 microseconds at 1100 K. Quantitative conversion to indene must occur.

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